Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds

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PREFACE

The work described in this dissertation was performed under the sponsorship of the Office of Naval Research.

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The Board of Control of this Institution has made an application for a patent on the invention contained herein.

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I. INTRODUCTION AND HISTORICAL NOTES

A. Literature Review

The phenomenon of ion exchange was first observed almost a century ago, in 1850, by J. Thomas Way, consulting chemist to the Royal Agricultural Society of England (21). Way wanted to know why water-soluble fertilizers such as ammonium sulfate or potassium chloride stayed in the soil and did not wash out when it rained. He put some soil in a vertical cylinder with an outlet at the bottom and poured over it a solution of ammonium sulfate, washing down with water. No matter how much wash water he used ammonium sulfate could not be found in the effluent. The first portions of liquid to come out contained calcium sulfate. If he poured potassium chloride in at the top, calcium chloride came out the bottom. In every case, the positive radical was retained by the soil, while the negative radical went through unaltered.

It was some fifty years after Way's discovery before ion exchange assumed any industrial importance. The first part of the twentieth century marked the beginning of zeolite water softening. The ion exchangers in use were the synthetic aluminosilicates or natural aluminosilicates.

The discovery of Adams and Holmes (1) that phenol when condensed with formaldehyde, and aromatic amines when condensed with formaldehyde would give synthetic resins with cation and anion exchange properties respectively, might be called the dawn of the modern era of ion exchange. This was the first time anion exchange reactions had been described. The improvements of anion exchange resins, since their original invention, have not been as numerous as those of cation exchangers.

The only successful commercial anion exchangers are organic in origin. The synthetic resins have proved superior to all known natural compounds with anion exchange properties. Even though only recently available, they have found many applications. The ion exchange process will not remove dissolved impurities which are not ionized such as sugar. Anion exchangers are, therefore, useful for removing dissolved salts from sugar juices. This is especially important in the beet sugar industry where the large electrolyte content of untreated juices interferes with the crystallization of the sugar. Reports (6, 22) have been published claiming a higher yield of sugar by using ion exchangers.

The problem of complete silica removal from water has long confronted the water profession. The deposit of silicates in boilers and turbines has increased in importance as boiler pressures and temperatures have continued to rise. The complete removal of the last traces of silica has been accomplished efficiently and also economically from water with anion exchange resins (4, 3). Silica is converted to fluosilicic acid and removed as such with an anion exchange resin.

Besides removing unwanted impurities, anion exchangers can be used to recover valuable substances. The main purpose of the anion exchange process in manufacture of apple sirup is the reduction of the acidity of apple juice, but in addition, l-malic acid can be obtained as a valuable by-product (9, 8). After being adsorbed on an anion exchanger, it can be recovered from the effluent from the sodium carbonate regeneration of the exchanger by precipitating it as the normal calcium salt. Then the free malic acid is obtained by a double decomposition reaction with sulfuric acid. Anion exchangers have been used in the recovery of tartaric acid from grape wastes (16, 15). The tendency of the exchanger to lose effectiveness from repeated contact with the complex grape waste solution does not permit low cost operation.

The recovery of chromium, molybdenum, vanadium, iron, and the precious metals, gold, palladium, and platinum by anion exchange has been reported (17, 20). The metal is first converted into a complex anion and then brought in contact with the exchanger. The metal can be obtained from the resin by either chemical means or ignition of the exhausted resin.

One of the more perplexing problems which has confronted the pharmaceutical industry is the isolation and purification of amino acids from protein hydrolyzates. Cannon (11, 10), Englis and Fiess (13), Cleaver *et al.* (12), and Block (5) have used both cation and anion adsorbents in separating into different groups the basic, neutral, and acidic amino acids. While the schemes so far tried have not given quantitative separation, nevertheless, ion exchangers offer a different treatment of a problem which to date has defied practical commercial solution.

Ion exchange has application in preparative chemistry. It can be used as a simple method for making colloidal suspensions of hydrous oxides (19). Dilute ferric sulfate solution passed through an alkali-regenerated anion exchanger gives a red ferric oxide sol.

Production of anion exchangers is quite small relative to the total ion exchange production. At the present they constitute only about 2% of the physical volume. It is reasonable to expect a continued expansion of resinous exchangers in the water treating field and in industry as new and more selective exchangers come out of the laboratories.

B. Statement of the Problem

The application of anion exchange has been limited, until recently, because of the unavailability of an exchange substance having sufficiently strong base characteristics which would permit the exchange of anions in neutral and alkaline media. The anion exchange resins that have been available are mostly of the weak base type. They have shown appreciable capacity for anion adsorption only in the pH range 1 to 5.

The absence of information in literature concerning the polymerization of unsaturated quaternary ammonium compounds prompted this study of the preparation and polymerization of compounds of this type as a possible source of water insoluble polymers containing strongly basic groups. Products of this nature containing insoluble cations, but holding ionizable anions should extend the scope of anion exchange to neutral and alkaline media as well as acid media.

C. Source and Purification of Reactants

Piperazine hexahydrate and piperidine, practical grade, were obtained from Eastman Kodak Company and used as received. The n-butyl amine, dibutyl amine, morpholine, and anhydrous ethylenediamine were obtained from Carbide and Carbon Chemical Company and used without further treatment. The diallyl amine, allyl chloride, β-methylallyl chloride, and di-tertiary-butyl peroxide were obtained through the courtesy of Shell Chemical Company. The allyl chloride was redistilled and the fraction boiling in the range 44.7-45.0°C was used in this work. The β-methylallyl chloride was redistilled. The fraction boiling between 71.5-72.5°C was recovered. The allyl bromide was obtained from Dow Chemical Company and used without further purification. The tertiary-butyl hydroperoxide was obtained as a 60% solution through the courtesy of Union Bay State Company.

II. PREPARATION OF UNSATURATED TERTIARY AMINES

A. General Discussion

Due to the fact that very few unsaturated tertiary amines are commercially available, it was necessary to prepare several of them as intermediates for the preparation of the unsaturated quaternary ammonium compounds. These amines were prepared by a modification of the procedure of Willson and Wheeler for benzyl aniline as outlined in Organic Syntheses (18).

The general method used by the author was the following: the secondary amine and 0.25 mole excess of sodium bicarbonate in an aqueous solution were placed in a three-necked, round-bottom flask fitted with a water-cooled reflux condenser, mechanical stirrer, and a separatory funnel. To the above mixture was added dropwise, with vigorous agitation, 0.05 mole excess of the appropriate alkyl or alkenyl halide. The mixture was maintained under gentle reflux with stirring for an average reaction time of 5 hours. The contents of the flask were filtered when cool and solid sodium hydroxide was added to the filtrate. The dry amine layer was purified by fractional distillation. A column 2 x 28 cm., packed with 1/4 inch Berl saddles was used. Since there was a large difference between the boiling-points of the reactants and the products, this column was very satisfactory. The heat necessary for distillation was supplied by an electrical heating mantle. To obtain good heat exchange between vapor and liquid, and to avoid flooding, the column, distilling pot, and head were well insulated with glass wool. Ground-glass joint equipment was used for both the preparation and purification of the amines.

Temperatures recorded for the boiling-points are uncorrected. Pressures greater than 10 mm. were measured by means of a Zimmerli gauge. Pressures below 10 mm. were measured by a McLeod gauge purchased from the Scientific Supply Company.

The refractive indexes were determined by means of an Abbé refractometer at 25°C. White light was used as the source of illumination. Constant temperature was maintained by circulating water through the refractometer from a constant temperature bath. Before taking a reading sufficient time was allowed for the amine to acquire the same temperature as the lens of the instrument.

The specific gravities were determined at 25°C with a carefully calibrated 10 ml. specific gravity bottle of the Leach type. The bottle was equipped with a capillary side tube with a ₮ cap. The thermometer, with a range of 14° to 36°C in 0.2° subdivisions, was also attached with a ₮ joint. In order to eliminate any source of error due to the compounds decomposing on standing, which is characteristic of unsaturated compounds, freshly distilled portions of the compounds were used in both the specific gravity and refractive index determinations. In all cases values were obtained at least in duplicate.

The nitrogen content of the amines was found by the Kjeldahl method. The usual Kjeldahl procedure of using cupric sulfate as a catalyst for accelerating the rate of digestion failed to give quantitative results with the cyclic compounds. Mercuric oxide as the catalyst proved very satisfactory. In this case the sodium hydroxide solution should contain two parts sodium thiosulfate to one part of mercuric oxide. The complex substances formed by mercuric sulfate and ammonia are not decomposed readily by alkali alone. Sodium thiosulfate is efficient for this purpose.

Since the number of unsaturated tertiary amines recorded in the literature is comparatively small, many of these intermediates were new compounds. The properties, analyses, and yields of these new tertiary amines and those which have been previously mentioned in literature, but without physical constants are summarized in Table I. Individual details not covered in this general discussion can be found in the experimental part of this section.

TABLE I

UNSATURATED TERTIARY AMINES

COMPOUND	FORMULA	B.P. °C/mm	D_{25}^{25}	N_D^{25}	ANALYSES %N		%
					CALCD.	FOUND	YIELD
N-Allyl morpholine[a]	$C_7H_{13}NO$	156-8/768	0.9267	1.4569	11.02	10.9	60
N,N'-Diallyl piperazine[b]	$C_{10}H_{18}N_2$	213/761	0.8865	1.4761	16.88	16.8	31
Diallyl benzyl amine	$C_{13}H_{17}N$	89/4	0.9109	1.5122	7.48	7.39	73
N-β-Methylallyl piperidine	$C_9H_{17}N$	165/760	0.8351	1.4559	10.06	9.88	42
N-β-Methylallyl morpholine	$C_8H_{15}NO$	171/760	0.9120	1.4555	9.91	9.74	61
Diallyl butyl amine[c]	$C_{10}H_{19}N$	170/760	0.7863	1.4389	9.14	9.11	53
N,N'-Di-β-methylallyl piperazine	$C_{12}H_{22}N_2$	235/760	0.8692	1.4710	14.42	14.1	52
Dibutyl allyl amine[d]	$C_{11}H_{23}N$	191-2/760	0.9889	1.4321	8.27	8.26	57
N,N,N',N'-Tetraallyl ethylenediamine	$C_{14}H_{24}N_2$	92/3	0.8517	1.4702	12.71	12.6	41

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[a] Picrate, m.p. 118°C; chloroplatinate, m.p., 183.5°C; picrolonate, m.p. 213°C.
[b] Picrate, m.p. 254°C; chloroplatinate, m.p., 280°C.
[c] Previously reported without physical constants (7).
[d] Previously reported without physical constants (2).

B. Experimental

Individual details not included in the general procedure are given in this section. All temperatures are in degrees centigrade, and its symbol is omitted in conformity with the present usage in scientific reports.

Synthesis of N-allyl morpholine.--This compound was prepared by three different methods: (1) reaction of morpholine and allyl bromide, (2) reaction of allyl amine and β,β' dichloroethyl ether, (3) reaction of morpholine and allyl chloride.

1. A mixture of 21.8 ml. of morpholine, 13 g. of sodium bicarbonate, and 10 ml. of water was placed in a 500 ml. flask. To this mixture was added dropwise, over a period of 1½ hours, 21.1 ml. of allyl bromide. The reaction was maintained at 60° throughout the reaction and stirred four additional hours after all the allyl bromide was added. Isolation procedure was the same as in the general discussion. The N-allyl morpholine was twice distilled. The amount of distillate boiling between 156-158°/768 mm. was 12 ml. or a yield of 34.9%.

   The following derivatives were prepared: (a) picrate, m.p. 118.0° corrected, (b) chloroplatinate, m.p. 183.5° corrected, (c) picrolonate, m.p. 213° corrected, (d) hydrochloride, too hygroscopic for m.p.

The molecular weight of N-allyl morpholine was determined from the chloroplatinate: Calcd. 127.12. Found: 127.8.

Analysis: Calcd. for $C_7H_{13}NO$: N, 11.02. Found: N, 10.9.

Physical Constants: D^{25}_{25} 0.9267; n^{25}_{D} 1.4569; b.p. 156-8° at 768 mm.

2. To a solution of 18 ml. of β,β-dichloroethyl ether, 168 g. of sodium bicarbonate, and 30 ml. of water heated to 58°, 77 ml. of allyl amine was added dropwise with stirring. The heating of the mixture was gradually increased from 58° to 120° as the reaction proceeded. The yield of N-allyl morpholine was 8.5 ml. or 6.0%. The melting point of the picrate and other physical constants corresponded with the previous listed data in method one.

3. Three hundred and seventy-seven milliliters of allyl chloride were added dropwise to 400 ml. of morpholine, 386.4 g. of sodium bicarbonate, and enough water to make a thin paste. After the ebullition of heat had ceased, the mixture was heated under gentle reflux for 45 minutes. Isolation and purification were carried out as outlined in the general discussion. A yield of 350 g. or 60% was obtained.

Synthesis of N,N'-diallyl piperazine.--N,N'-diallyl piperazine was prepared by adding dropwise 131 ml. of allyl bromide to a solution of 97 g. of piperazine hexahydrate, 101 g. of sodium bicarbonate, and 50 ml. of water. The temperature of the reaction was increased from 80° to 150° over a period of three hours as the reaction proceeded. Isolation and purification were performed as outlined in the general discussion. The yield based on piperazine was 31%.

The following derivatives were prepared: (a) picrate, decomposes and then liquifies at 254° corrected, (b) chloroplatinate, decomposes at 280° corrected. The molecular weight of N,N-diallyl piperazine was determined from the chloroplatinate. Calcd. 166.3. Found: 167.8.

Analysis: Calcd. for $C_{10}H_{18}N_2$: N, 16.88. Found: N, 16.8.

Physical Constants: D^{25}_{25} 0.8865; n^{25}_D 1.4761, b.p. 213° at 761 mm.

Synthesis of N-β-methylallyl morpholine.--To a mixture of 84 g. of sodium bicarbonate, and 87 ml. of morpholine in 75 ml. of water was slowly added 98 ml. of β-methylallyl chloride. The mixture was allowed to warm until the reaction started, and then the flow of β-methylallyl chloride was regulated in order not to overtax the reflux condenser. No external heat need be applied for this reaction. When the reaction had cooled, the isolation and purification were accomplished in the regular manner. The yield of N-β-methylallyl morpholine, b.p. 171° at 760 mm., was 86 g. (61%).

Analysis: Calcd. for $C_8H_{15}NO$: N, 9.91. Found: N, 9.74.

Physical Constants: D^{25}_{25} 0.9120; n^{25}_D 1.4555, b.p. 171° at 760 mm.

Synthesis of diallyl butyl amine.--One hundred and seventy grams of sodium bicarbonate mixed with water to form a thin paste and 300 ml. of butyl amine were placed in a flask. To this was added dropwise with stirring 497 ml. of allyl chloride. The mixture was heated under gentle reflux for a total of two hours. Isolation and purification were carried out according to the general procedure. The total yield of diallyl butyl amine was 154 g. (33.2%). The above procedure was repeated later with a total reflux time of four hours. In this case 210 g. or 47.4% yield was obtained. Diallyl butyl amine has been reported previously in literature without physical constants (7).

Analysis: Calcd. for $C_{10}H_{19}N$: N, 9.14. Found: N, 9.11.

Physical Constants: D^{25}_{25} 0.7863; n^{25}_{D} 1.4389, b.p. 170° at 760 mm.

Synthesis of N,N'-di-β-methylallyl piperazine.--A solution of 50 ml. of water, 168 g. of sodium bicarbonate, and 194 g. of piperazine hexahydrate was warmed to 50° and 196 ml. of β-methylallyl chloride was dropped in over a period of one hour. The temperature of the mixture was maintained at 50° during the addition and then gradually raised to 110°. The total time of heating was five hours. The method of isolation and purification conformed to the general procedure. After redistilling the main fraction, 101 g. or a yield of 52% of pure N,N'-di-β-methylallyl piperazine was obtained. It had a boiling point of 235° at 760 mm.

Analysis: Calcd. for $C_{12}H_{22}N_2$: N, 14.42. Found: N, 14.1.

Physical Constants: D^{25}_{25} 0.8692; n^{25}_{D} 1.4710, b.p. 235° at 760 mm.

Synthesis of N-β-methylallyl piperidine.--To a mixture of 126 g. of sodium bicarbonate, 50 ml. of water and 150 ml. of piperidine, 146 ml. of β-methylallyl chloride was added dropwise. Vigorous agitation was maintained throughout the reaction. The mixture was allowed to warm until the reaction began to reflux, and then the rate of flow of the β-methylallyl chloride was regulated so as to maintain only gentle reflux. When the ebullition of heat had ceased, the isolation and purification were executed in the regular manner. The yield in this reaction was 87g. (42%) of N-β-methylallyl piperidine.

Analysis: Calcd. for $C_9H_{17}N$: N, 10.06. Found: N, 9.88.

Physical Constants: D^{25}_{25} 0.8351; n^{25}_{D} 1.4559, b. p. 165° at 760 mm.

Synthesis of diallyl benzyl amine.--Sixty-four grams of diallyl amine, 53 g. of sodium bicarbonate, and 50 ml. of water were heated on a steam bath while 58 ml. of benzyl chloride was added dropwise over a period of one and a half hours. The mixture was heated for a total of four hours. Isolation and purification were carried out in the normal manner. After twice distilling the amine layer, 69 g. of diallyl benzyl amine or a yield of 73% was isolated. The boiling point was found to be 88-9° at 3 to 4 mm.

Analysis: Calcd. for $C_{13}H_{17}N$: N, 7.48. Found: N, 7.39.

Physical Constants: D^{25}_{25} 0.9109; n^{25}_{D} 1.5122, b.p. 88-9° at 3 to 4 mm.

Synthesis of allyl dibutyl amine.--To prepare allyl dibutyl amine, 150 ml. of dibutyl amine was added to a watery paste of 74.7 g. of sodium bicarbonate, and to this solution 77.7 ml. of allyl bromide was added dropwise with stirring. There was a slight ebullition of heat. After this heat had subsided, the mixture was heated under gentle reflux for one hour. The mixture was cooled, filtered, and solid sodium hydroxide added to the filtrate. The amine layer was separated and then dried over solid sodium hydroxide. Upon distilling, the first fraction came over at 110-190°/760 mm. and then the main fraction at 191-192°/760 mm. Most of the lower fraction, after vigorous drying with solid sodium hydroxide, was found to distill also at 191-192°. A total yield of 96.5 g. or 57% was obtained.

Since Adams (2) had listed the boiling point of allyl dibutyl amine as 185-7.5, without other physical data, a nitrogen analysis was run to test the purity of the compound. The analysis below bears out the fact the compound was pure allyl dibutyl amine.

Analysis: Calcd. for $C_{11}H_{23}N$: N, 8.27. Found: 8.26.

Physical Constants: D^{25}_{25} 0.9889; n^{25}_{D} 1.4321, b.p. 191-2° at 760 mm.

Synthesis of N,N,N',N'-tetraallyl ethylenediamine.--This compound was prepared by three different methods: (1) reaction of ethylene dibromide and diallyl amine, (2) reaction of ethylenediamine and allyl bromide in water, (3) reaction of ethylenediamine and allyl bromide in n-propyl alcohol.

1. Sixty milliliters of ethylene dibromide were added dropwise to 138 g. of diallyl amine and a watery paste of 135 g. of sodium bicarbonate. The mixture was heated under gentle reflux for nine hours. The amine layer was fractionated and the main fraction distilled twice. This main fraction gave a yield of 63 g. (41%) of N,N,N',N' tetraallyl ethylenediamine boiling at 92°/3 mm. A variation of ½ mm. will change the boiling point 1° at this low pressure.

   Analysis: Calcd. for $C_{14}H_{24}N_2$: N, 12.71. Found: N, 12.6.

   Physical Constants: D^{25}_{25} 0.8517; n^{25}_{D} 1.4702, b.p. 92° at 3 mm.

2. One hundred milliliters of ethylenediamine and a watery paste of 504 g. of sodium bicarbonate were stirred while 517 ml. of allyl bromide was added dropwise. The reaction was kept under gentle reflux for six hours, cooled, filtered, and solid sodium hydroxide added to the filtrate. The amine layer did not separate very well, but tended to emulsify. To the amine-water solution, 200 ml. of n-propyl alcohol was added, and on standing small needle crystals separated. They were filtered off, washed with dry ether, and dried. They weighed 55 g. A portion of the solid was recrystallized from ethyl alcohol three times, and dried in a pistol dryer at 100°/10 mm. This substance had a m.p. 142° and a bromide analysis of 34.28% as compared with 34.57% for hexaallyl ethylenediammonium dibromide. From repeated distillation of various fractions, the main fractions isolated were: (1) 30 grams b.p. 148-150°/760 mm. with a nitrogen content of 10.4%. This was not within range of any of the possible substitution products. (2) 42 grams, b.p. 215-216°/760 mm. with a nitrogen content of 15.2%. This was probably N,N,N'-triallyl ethylenediamine which has 15.4% nitrogen. (3) 40 grams or 12.1% yield boiling at 92°/3 mm. The physical constants of this fraction checked with the previously prepared N,N,N',N'-tetraallyl ethylenediamine.

No attempt was made to further identify the lower boiling fractions.

3. Normal propyl alcohol was added to 504 g. of sodium bicarbonate and 100 ml. of anhydrous ethylenediamine to form a thin paste. To this mixture, 721 ml. of allyl bromide was added dropwise with stirring. The mixture was heated under gentle reflux for a total of three hours. The sodium bromide was filtered off when the mixture had cooled. Then most of the solvent was removed by distillation under aspirator pressure. The residue was filtered, transferred to a round-bottom flask, and fractionated under reduced pressure. Two main fractions were isolated: (1) 39 g. boiling at 130-148°/760 mm. Most of it came over at 147°. The nitrogen content of the portion boiling at 147° was 13.2%. This percentage does not correspond to the nitrogen content of any of the possible substitution products. (2) 58 g. or 17% yield of N,N,N',N'-tetraallyl ethylenediamine boiling at 92°/3 mm. The physical constants were the same as previously listed in method one.

III. PREPARATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES

A. General Discussion

All of the quaternary ammonium halides were prepared by substantially the same method. The general procedure was to add dropwise with stirring an equimolecular quantity of the alkyl or alkenyl halide to the unsaturated tertiary amine dissolved in acetophenone. If the reaction was not exothermic, the mixture was held at reflux temperature until considerable solid material was observed on the cooler portion of the reaction vessel. In most cases, the products were insoluble in the solvent and crystallized on cooling. The product was collected and washed with dry ether. Dry ether was also added to the mother liquid in order to recover any product that was soluble in it. Purification was accomplished by repeated recrystallization from alcohols, chloroform-ether, or formamide-acetone mixtures. In many cases eight to ten recrystallizations were necessary before there was no change in the melting point on further recrystallization. The ether used for recrystallization must be absolutely dry to prevent loss of product. The ether was first dried over calcium chloride and then the last traces of moisture were removed by placing the ether in the presence of sodium ribbon. The ether was filtered before use.

The halogen content of the quaternary ammonium salts was found by direct titration with a 0.1 normal solution of silver nitrate. The bromides were titrated with eosin as an indicator. The color change to red was extremely sharp. Dichlorofluorescein was used as an indicator for the titration of the chlorides. The end-point was a sudden change from white to pink in the color of the silver chloride particles. Dextrin was used to prevent coagulation of the silver halides. A 10 ml. buret with 0.02 ml. subdivisions was used.

The procedure was to weigh three 0.05 to 0.1 g. samples of the quaternary ammonium halide into 125 ml. Erlenmeyer flasks. These were dissolved in 20 ml. of distilled water and about 0.05 g. of dextrin and 3 drops of indicator were added. The solutions were titrated with silver nitrate in diffuse light. The indicator blank was negligibly small.

The melting points were determined by the open capillary-tube method with the aid of a copper melting point block. The thermometer used was calibrated in this melting point block against a series of Anschütz thermometers previously calibrated by the Bureau of Standards.

The majority of the compounds were prepared as the bromides. In the pure state, they were white deliquescent solids with rather high melting points. The introduction of relatively high molecular weight radicals, such as benzyl, usually lowered the melting point. The salts are very soluble in water, low molecular weight alcohols, formamide and warm ketones. The products were stored under anhydrous conditions to prevent absorption of moisture.

The properties, analyses, and yields of these new quaternary ammonium halides are summarized in Table II. Individual details are discussed in the experimental part of this section.

TABLE II

UNSATURATED QUATERNARY AMMONIUM HALIDES

BROMIDE	FORMULA	M.P. °C	ANALYSES CALCD.	% Br. FOUND	% YIELD
Triallyl ethyl ammonium	$C_{11}H_{20}BrN$	159	32.47	32.65	77
Triallyl butyl ammonium	$C_{13}H_{24}BrN$	175	29.14	28.98	77
Diallyl morpholinium	$C_{10}H_{18}BrNO$	213	32.21	32.30	89
Tetraallyl piperazinium di-	$C_{16}H_{28}Br_2N_2$	207	39.25	39.26	67
Tetraallyl ammonium[a]	$C_{12}H_{20}BrN$	185	30.95	31.07	69
Diallyl piperidinium	$C_{11}H_{20}BrN$	190[b]	32.47	32.64	79
Triallyl benzyl ammonium	$C_{16}H_{22}BrN$	132	25.93	25.70	71
Allyl-β-methylallyl morpholinium	$C_{11}H_{20}BrNO$	197	30.48	30.56	53
Allyl-β-methylallyl piperidinium	$C_{12}H_{22}BrN$	195.5	30.71	31.10	72
Di-β-methylallyl piperidinium	$C_{13}H_{24}BrN$	175	29.14	29.21	63
Diallyl morpholinium[c]	$C_{10}H_{18}ClNO$	180	17.41	17.29	65
Hexallyl ethylenediammonium di-	$C_{20}H_{34}Br_2N_2$	142	34.57	34.28	90
Diallyl di-β-methylallyl piperazinium di-	$C_{18}H_{32}Br_2N_2$	182	36.63	36.57	54

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[a] Previously reported as decomposing at 80°C (14).
[b] This is a flash m.p.; no true melting point on slow heating.
[c] The compound prepared was the chloride, and the analytical values are % chlorine.

B. Experimental

Synthesis of triallyl ethyl ammonium bromide.--One-tenth of a mole of allyl bromide was added dropwise with stirring to 0.1 mole of diallyl ethyl amine dissolved in 15 ml. of acetophenone. The solid product was filtered, washed with dry ether, and recrystallized from chloroform. Yield: 77%; m.p. 159°. Analysis: Calcd. for $C_{11}H_{20}BrN$: Br, 32.47. Found: Br, 32.65.

Synthesis of triallyl butyl ammonium bromide.--Nine-tenths of a mole of allyl bromide was added dropwise with stirring to 0.9 mole of diallyl butyl amine, using 50 ml. of acetophenone as solvent. A small amount of heat was applied to start the reaction. The product was filtered, washed with dry ether, and recrystallized from ethyl alcohol. Yield: 77%; m.p. 175°. Analysis: Calcd. for $C_{13}H_{24}BrN$: Br, 29.14. Found: 28.98.

Synthesis of diallyl morpholinium bromide.--One and six-tenths moles of allyl bromide were added dropwise to a solution of 1.6 moles of N-allyl morpholine and 100 ml. of acetophenone heated to 80°. The reaction was completed soon after the addition of the allyl bromide. The product was purified by recrystallization from ethyl alcohol. Yield: 89%; m.p. 213°. Analysis: Calcd. for $C_{10}H_{18}BrNO$: Br, 32.21. Found: 32.30.

Synthesis of tetraallyl piperazinium dibromide.--To a mixture of 0.015 mole of N,N'-diallyl piperazine and 15 ml. of acetophenone heated to 80°, 0.03 mole of allyl bromide was added dropwise. The temperature of the reaction was increased slowly from 80° to 170° as the reaction proceeded. The white crystalline solid was recrystallized from ethyl alcohol. Yield: 67%; m.p. 207°. Analysis: Calcd. for $C_{16}H_{28}Br_2N_2$: Br, 39.25. Found: 39.26.

Synthesis of tetraallyl ammonium bromide.--This compound was prepared by adding dropwise 0.495 mole of allyl bromide to 0.495 mole of triallyl amine in 100 ml. of acetophenone. The mixture was kept at 78° for two hours. The solid was filtered, washed with ether, and recrystallized from chloroform. Yield: 69%; m.p. 185°. Analysis: Calcd. for $C_{12}H_{20}BrN$: Br, 30.95. Found: 31.07. This compound has been reported as decomposing at 80° (14).

Synthesis of diallyl piperidinium bromide.--Two-tenths of a mole of allyl bromide was added slowly to 0.2 mole of N-allyl piperidine dissolved in 25 ml. of acetophenone. The solid was filtered, and purified by recrystallization from a mixture of chloroform and ether. The pure compound slowly decomposed on gradual heating. A series of melting point tubes were filled. One was placed in the melting point block at each degree rise in temperature. This compound was found to have a sharp flash melting point of 190°. Yield: 79%; m.p. 190°. Analysis: Calcd. for $C_{11}H_{20}BrN$: Br, 32.47. Found: 32.64.

Synthesis of triallyl benzyl ammonium bromide.--One-tenth of a mole of allyl bromide was added dropwise to a solution of 0.1 mole of diallyl benzyl amine and 20 ml. of acetophenone. The mixture was warmed gently during the addition of the allyl bromide. The reaction was allowed to cool, filtered, and the solid product washed with dry ether. The product was recrystallized from ethyl alcohol. Triallyl benzyl ammonium bromide was also prepared by the reaction of triallyl amine with benzyl bromide. In the latter case the reaction was exothermic. Yield: 71%; m.p. 132°. Analysis: Calcd. for $C_{16}H_{22}BrN$: Br, 25.93. Found: Br, 25.70.

Synthesis of allyl-β-methylallyl morpholinium bromide.-To a solution of 0.082 mole of N-β-methylallyl morpholine and 10 ml. of acetophenone was added dropwise 0.082 mole of allyl bromide. The mixture was maintained at 90° for one and one-half hours. The solid product was purified by dissolving in chloroform and salting it out with ether. Yield: 53%; m.p. 197°. Analysis: Calcd. for $C_{11}H_{20}BrNO$: Br, 30.48. Found: 30.56.

Synthesis of allyl-β-methylallyl piperidinium bromide.-Seventeen-hundredths of a mole of allyl bromide was added dropwise with agitation to 0.17 mole of N-β-methylallyl piperidine in 10 ml. of acetophenone. The mixture was heated slightly to start the reaction which proceeded without further heating. The solid product was purified by dissolving in chloroform and salting out with ether. Yield: 72%; m.p. 195.5°. Analysis: Calcd. for $C_{12}H_{22}BrN$: Br, 30.71. Found: 31.10.

Synthesis of diallyl di-β-methylallyl piperazinium dibromide.--Two-tenths of a mole of allyl bromide was added dropwise with stirring to 0.1 mole of N,N'-di-β-methylallyl piperazine in 20 ml. of acetophenone. The mixture was heated at 95° for one hour after the addition of the allyl bromide. The white solid which separated was purified by dissolving in ethyl alcohol and salting out with ether. Yield: 54%; m.p. 182°. Analysis: Calcd. for $C_{18}H_{32}Br_2N_2$: Br, 36.63. Found: 36.57.

Synthesis of di-β-methylallyl piperidinium bromide.--One-tenth of a mole of β-methylallyl bromide was added dropwise with stirring to a solution of 0.1 mole of N-β-methylallyl piperidine in 10 ml. of acetophenone. The reaction was heated under gentle reflux for one and one-half hours. The solid product which separated was purified by recrystallation from ethyl alcohol. Yield: 63%; m.p. 175°. Analysis: Calcd. for $C_{13}H_{24}BrN$: Br, 29.14. Found: Br, 29.21.

Synthesis of diallyl morpholinium chloride.--One and five-tenths moles of N-allyl morpholine and 50 ml. of acetophenone were placed in a flask. To this was added 1.5 moles of allyl chloride. The mixture was stirred and refluxed for one and one-half hours. Only a small amount of solid settled out over night. The mixture was then transferred to a rocking autoclave and subjected to 110° for two hours. The product was purified by recrystallation from ethyl alcohol. Yield: 65%; m.p. 180°. Analysis: Calcd. for $C_{10}H_{18}ClNO$: Cl, 17.41. Found: 17.29.

Synthesis of hexaallyl ethylenediammonium dibromide.- Fifty milliliters of acetophenone and 0.26 mole of N,N,N',N'-tetraallyl ethylenediamine were mixed and to this was added, with stirring, 0.52 mole of allyl bromide. The mixture was maintained at 105° for six hours. The product was washed with dry ether and recrystallized from ethyl alcohol. Yield: 90%; m.p. 142°. Analysis: Calcd. for $C_{20}H_{34}Br_2N_2$: Br, 34.57. Found: 34.28.

IV. POLYMERIZATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES

A. General Discussion

It is a well-known fact that small amounts of hydroquinone or diphenylamine are capable of preserving such monomers as styrene, vinyl acetate, and dienes. It is further believed that peroxide catalyzed polymerizations proceed by a free radical chain reaction. Such a mechanism would be subject to strong inhibition by small amounts of diphenylamine or other similar substances. In view of these facts, there was some doubt that polymerization of quaternary ammonium halides could be accomplished. This was found not to be the case as will be described later.

The introduction of cross linking into the molecule leads gradually to polymeric products with decreased solubilities. The more unsaturated groups there are the better chance of getting cross-linked polymers. Therefore, all the compounds studied have contained from two to six unsaturated groups.

The difficulty of producing exchange resins is that groups which impart exchange properties tend to increase the solubility of the resin, while groups which promote insolubility do not have ion exchange characteristics. One must then accept a resin between these two extremes. A resin with a high exchange capacity, showing slight swelling in solvents, would be more useful than one with a low capacity, yet impervious to solvents.

The choice of a catalyst for the polymerization would appear to be an easy one, since the quaternary ammonium salts are very soluble in water. Commonly used water soluble catalysts, such as hydrogen peroxide and ammonium persulfate, should be ideal. Attempts to obtain polymerization of aqueous solutions of the compounds using these catalysts were unsuccessful. Benzoyl peroxide and di-tertiary-butyl peroxide were also tried without success. Tertiary-butyl hydroperoxide was found to be the most effective catalyst in initiating the polymerization reaction.

In order to control the heat evolved in the polymerization reactions and to form a polymer of high molecular weight, it is necessary to have the lowest initiating temperature possible. The high melting points of the quaternary ammonium halides made it necessary to attempt polymerization either in solution, or by the addition of some component to lower the melting points. A few drops of water or formamide proved very valuable to reduce the temperature required for polymerization. By the use of formamide, the polymerization of a highly unsaturated compound such as hexaallyl ethylenediammonium dibromide could be performed at 70°. Addition of suitable components for lowering the melting points to a desirable range was accomplished by preparing mixtures of the higher melting compounds with triallyl benzyl ammonium bromide which had a melting point of 132°. Mixtures were obtained which fused to a liquid in the range of 85-90°. Copolymerization also resulted in the combination of the desirable qualities of the two separate products.

The temperature, the solvent, etc. affect the nature of the polymer. For example, if many active centers are formed, as would be the case with a large amount of catalyst, the monomer would be divided between all of them and the chain length of the polymer would not be great. In order to obtain desirable products several polymerizations had to be run in which only one of the above mentioned variables was changed at a time to see their effect on the polymer. The general procedure was to place the quaternary ammonium halide in a small beaker and add varying amounts of solvent and 60% tertiary-butyl hydroperoxide. This mixture was mixed well before being placed in an oven at a set temperature for a specific time.

A typical example of a polymerization will illustrate the method and also show how the ion exchange properties of the resin were demonstrated. Ten grams of tetraallyl ammonium bromide, 0.94 g. of formamide, and 0.22 g. of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 75°. Fusion was complete at this temperature. In about ten minutes the liquid had turned to a light brown, glassy solid. The sample was allowed to remain in the oven at 75° for twenty hours. The polymer was removed and hot distilled water added. The polymer failed to dissolve in the water, but was broken down to small insoluble particles. The resin was then washed with hot distilled water until the filtrate did not give a test for bromide. The polymer was then treated with 4% sodium hydroxide at room temperature and filtered. The filtrate, after being acidified with halogen-free nitric acid, gave a precipitate of silver bromide upon the addition of silver nitrate. This showed the polyquaternary ammonium bromide was being converted to the polyquaternary ammonium hydroxide. This treatment was continued until the acidified filtrate no longer gave a precipitate of silver bromide. A sodium fusion was run on a portion of the dried polymer and the filtrate tested for halogen. No precipitate of silver bromide was formed, indicating the halogen ions in the polymer had been replaced by hydroxyl ions. The converted resin was then washed free of sodium hydroxide as determined by adding phenol red indicator to the washings. Upon treating this converted polymer with 0.01 N sodium chloride solution, a strongly basic filtrate was obtained. This showed the hydroxyl ions had been replaced by the chloride ions.

The complete cycle may be illustrated in the following series of reactions:

$$nR_4NBr \xrightarrow[\text{hydroperoxide}]{\text{t-butyl}} (R_4NBr)_n$$

$$(R_4NBr)_n + nNaOH \longrightarrow (R_4NOH)_n + nNaBr$$

$$(R_4NOH)_n + nNaCl \longrightarrow (R_4NCl)_n + nNaOH$$

The polymers prepared ranged from water soluble ones to hard glassy ones impervious to solvents.

B. Experimental

The following experiments will serve to illustrate the methods of polymerization of the quaternary ammonium halides. Details are given in parts by weight. The polymeric quaternary salts required no purification after polymerization other than washing with water.

Copolymer of triallyl butyl ammonium bromide and diallyl morpholinium bromide.--One part of triallyl butyl ammonium bromide, 0.079 parts of water, and 0.044 parts of 60% t-butyl hydroperoxide were mixed well. The mixture was heated in an oven at 100° for 18 hours and at 125° for 6 hours. A hard, brittle, water insoluble polymer resulted. A 50% yield was obtained when washed free of water soluble matter. The polymer will undergo ion exchange reactions.

Copolymer of triallyl butyl ammonium bromide and tetraallyl ammonium bromide.--One part of triallyl butyl ammonium bromide, one part of tetraallyl ammonium bromide, 0.158 parts of water and 0.044 parts of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 85° for 13 hours, and then 11 hours at 110°. The sample appeared to be polymerized in 30 minutes. A light brown brittle water insoluble polymer was obtained. A yield of 67.5% was obtained after washing free of soluble materials and drying. The polymer will undergo ion exchange reactions.

Copolymer of triallyl benzyl ammonium bromide and tetraallyl ammonium bromide.--One part of triallyl benzyl ammonium bromide, one part of tetraallyl ammonium bromide, 0.158 parts of water, and 0.044 parts of 60% t-butyl hydroperoxide were heated in an oven at 80° for 17 hours. The temperature was then raised to 110° and held for 12 hours. The polymer showed very little swelling in hot water, and 56.4% was water-insoluble. The polymer will undergo ion exchange reactions.

Copolymer of tetraallyl ammonium bromide and diallyl piperidinium bromide.--One part of tetraallyl ammonium bromide and one part of diallyl piperidinium bromide was heated to 90°, and then 0.006 parts of 60% t-butyl hydroperoxide was added. The temperature rose from 90° to 132°. A rubber-like substance resulted, which turned to a light brown hard solid on cooling. It was water insoluble and will undergo ion exchange reactions.

Copolymer of diallyl morpholinium bromide and tetraallyl ammonium bromide.--One part of diallyl morpholinium bromide, and one part of tetraallyl ammonium bromide was heated in an oil bath to 100°. Then 0.012 parts of 60% t-butyl hydroperoxide was added. The temperature rose from 100° to 138°, indicating polymerization. The polymer was washed with water and dried. A yield of 83% was obtained. The polymer will undergo ion exchange reactions.

Copolymer of triallyl benzyl ammonium bromide and diallyl di-β-methylallyl piperazinium dibromide.--One part triallyl benzyl ammonium bromide and one part of diallyl di-β-methylallyl piperazinium dibromide was fused at 100°. Then 0.006 parts of 60% t-butyl hydroperoxide was added. Upon the addition of the catalyst the temperature rose from 100° to 132°. A brown, viscous, water-insoluble polymer resulted. Ion exchange reactions were not carried out, since the polymer was a liquid.

Polymer of tetraallyl ammonium bromide.--One part of tetraallyl ammonium bromide, 0.094 parts of formamide, and 0.022 parts of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 75°. The mixture became dark brown and glassy within 10 minutes. The temperature was held at 75° for 20 hours. A granular, water-insoluble substance was obtained after washing with hot water. A yield of 76% was obtained. The polymer will undergo ion exchange reactions.

Polymer of diallyl morpholinium bromide.--One part of diallyl morpholinium bromide, 0.021 parts of 60% t-butyl hydroperoxide, and 0.059 parts of formamide were mixed well and placed in an oven at 100° for 26 hours. On removal the mixture was hard and glassy. The polymer was water-soluble, indicating very little cross-linking took place. The procedure was repeated using water as a solvent, but only a water soluble polymer was obtained.

Polymer of hexaallyl ethylenediammonium dibromide.--One part of hexaallyl ethylenediammonium dibromide, 0.128 parts of formamide, and 0.022 parts of 60% t-butyl hydroperoxide were mixed well and placed in the oven at 70° for 17 hours. The polymer failed to dissolve in water, but was broken down to small insoluble particles. A yield of 55% was obtained. The polymer will undergo ion exchange reactions.

Polymer of di-β-methylallyl piperidinium bromide.--One part of di-β-methylallyl piperidinium bromide, 0.299 parts of formamide, and 0.022 parts of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 100° for 26 hours. On removal it was a hard glassy polymer; however, it was soluble in water. Evidently no cross-linking took place.

Polymer of triallyl butyl ammonium bromide.--One part of triallyl butyl ammonium bromide, 0.039 parts of water, and 0.011 parts of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 100°. After 12 hours, the temperature was raised to 125° for 12 hours. On washing with hot water, 52.5% yield of a light brown, granular water-insoluble polymer was obtained. The polymer will undergo ion exchange reactions.

V. DETERMINATION OF ION EXCHANGE CAPACITY

A. General Discussion

Although considerable progress has been made, one important aspect of ion exchange has been grossly neglected. This aspect involves the task of standardization of the test methods and terminology. Many of the methods that are now being used were set up for siliceous exchangers and designed for water-softening practices. However, since exchangers are now available that exhibit properties entirely different from those shown by siliceous exchangers, and since there are many other uses for exchangers outside of the water-softening field a need exists for a standardization of test methods and terminology. It is hoped that some organization such as the American Society for Testing Materials will undertake this project in the near future. The non-conformity of methods may be illustrated by considering how the capacity is expressed. Some base the capacity on a settled volume of the wet resin while others use a tamped volume of wet resin. A third way is to base the capacity on the weight of dry resin before conversion.

The pyrolysis of quaternary ammonium halides results in the formation of tertiary amines. If enough heat was evolved in the polymerization of the quaternary ammonium halides to cause pyrolysis, a certain amount of amine groups would be present in the resin. One may then picture the resins as not only having exchangeable anions, but also containing amine groups which would function in aqueous media as soluble amines. The capacities of resins of this type could be determined either as total capacity or as individual capacities.

The method used for determination of the capacity of the resins was a combination of various methods so that not only could the quaternary exchange capacity, and amine capacity be measured, but also an indication of the ease of replacement of the anions could be ascertained. This was done by titrating the resin electrometrically. The pH was taken at time intervals instead of at equilibrium conditions.

First, the polyquaternary ammonium halides were converted to the polyquaternary ammonium hydroxides. The conversion or metathesis was carried out by treating the resins with a large excess of 4% solution of sodium hydroxide. This may be done either by successive batch treatments or by passing the solution through a column of the resin. The latter procedure was preferable, since it gave a more nearly complete conversion in less time and required less of the sodium hydroxide solution. As the treatment was continued, the fraction of the exchanger in the desired form approached unity, asymptotically. This treatment was continued until the acidified effluent was found to be halogen-free.

The apparatus used consisted of a glass tube 12 mm. in diameter, closed at one end by a 50 mesh metal disk upon which the resin bed rested, and a means of introducing solutions into the top of the column. The open end of the effluent tube was above the top of the resin bed to prevent the liquid head from dropping below the top of the resin bed.

When the effluent, after acidifying with halogen-free nitric acid, no longer gave a precipitate of silver halide upon the addition of silver nitrate, the resins were washed free of sodium hydroxide. This was determined by adding a few drops of phenol red indicator to the washings. The resins in this form were ready for evaluation. As will be shown later, drying in an oven at 101° resulted in decomposition of the exchangers. Due to this fact the evaluations were based on a measured settled volume of the resins instead of on the weight of dry resins. The choice of a settled volume of wet resin seems to be a logical one. Most exchangers are used in some form of tanks or beds. The cost of construction of various size tanks or beds and the space occupied by them would be a prime factor. From a commercial standpoint capacity per milliliter of resin would be more valuable than capacity per gram of resin before conversion.

Samples of the converted resins were placed in 400 ml. beakers and 200 ml. of 0.01 M sodium chloride added. The resins were then titrated electrometrically with normal hydrochloric acid. One milliliter of acid was added at a time and the pH was taken at 3 minute intervals just prior to the addition of another milliliter of acid. The pH was plotted against milliliters of acid added and the titration curves drawn. The capacities of the resins calculated from these curves are summarized in Table III.

In order to determine the stability of the converted resins in the dry form, a sample of a freshly converted resin was divided into two equal portions. The first portion was titrated without drying. The second portion was dried in an oven at 101° for 12 hours. The resin was then soaked in distilled water and titrated. It can readily be seen from Graph I that the capacity of the resin was greatly decreased. This was also found to be the case with another resin tested. This is shown in Graph II.

Although true kinetic measurements were not made, the rate of exchange for these resins appears to be rapid. The three minute intervals between pH measurements was for all practical purposes sufficient time. The change in pH was very rapid at first, but little change occurred between the second and third minutes in the interval between measurements.

TABLE III.

CAPACITY OF RESINS

Polymer or Copolymer	Amine Capacity m.eq./ml.	Quaternary Cap. m.eq./ml.
Tetraallyl ammonium bromide[a]	0.12	0.32
Tetraallyl ammonium bromide[b]	0.084	0.40
Triallyl butyl ammonium bromide	-----	0.15
Hexaallyl ethylenediammonium dibromide[c]	0.11	0.25
Hexaallyl ethylenediammonium dibromide[d]	-----	0.29
Triallyl butyl ammonium bromide Tetraallyl ammonium bromide	-----	0.25
Diallyl morpholinium bromide Tetraallyl ammonium bromide	-----	0.27
Diallyl piperidinium bromide Tetraallyl ammonium bromide	-----	0.26

[a] Polymerized in formamide at 70°.
[b] Polymerized in water at 70°.
[c] Polymerized at 75°.
[d] Polymerized at 70°.

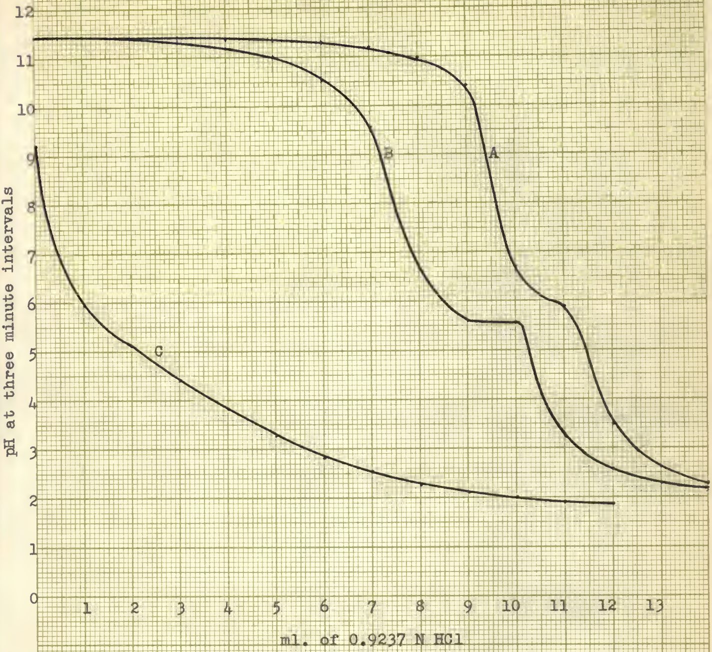
B. Experimental

The hydrochloric acid used in the evaluation of the resins was standardized gravimetrically by precipitation of silver chloride from a solution of silver nitrate. The silver chloride precipitate was digested, cooled, and filtered through a filtering crucible. The precipitate was dried in an oven at 130° until a constant weight was obtained. From the weight of silver chloride the normality of the acid was calculated.

The titrations were run with a Beckman Model H - 2 pH Meter. A glass electrode, Beckman #4990, and a calomel electrode, Beckman #4970 were used. The instrument was allowed a 15 minute warm-up period before proceeding with any measurements. The meter was standardized against a standard buffer solution before each series of titrations. During the measurements the standardization control was used to bring the meter needle into coincidence with the pointer before taking a reading.

The experimental results obtained in the evaluation of resins are shown in Graphs I, II, III. Twenty-two milliliters of resin measured as settled volume in distilled water were used in all the titrations.

GRAPH I.



Legend:

A. Polymer of tetraallyl ammonium bromide polymerized in water at 70°.

B. Polymer of tetraallyl ammonium bromide polymerized in formamide at 70°.

C. Polymer of tetraallyl ammonium bromide polymerized in water at 70° and dried in the hydroxide form at 101° before titration.

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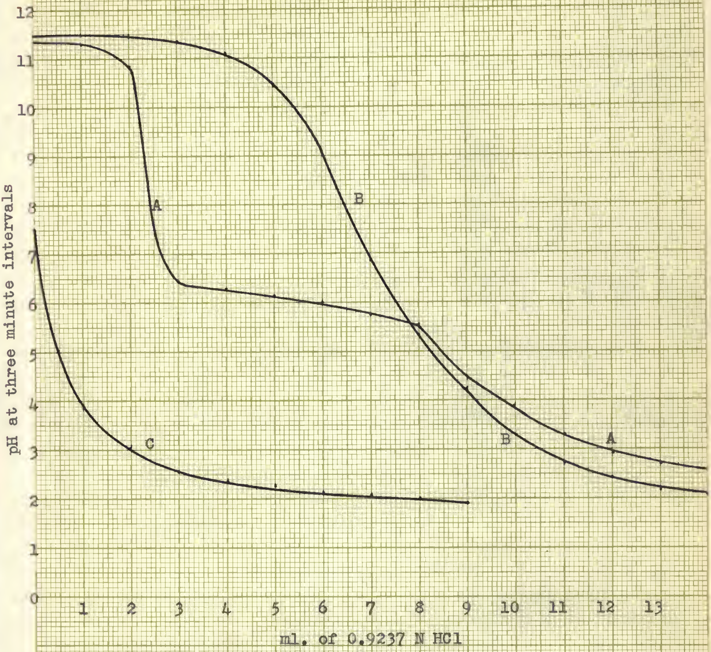
GRAPH II.



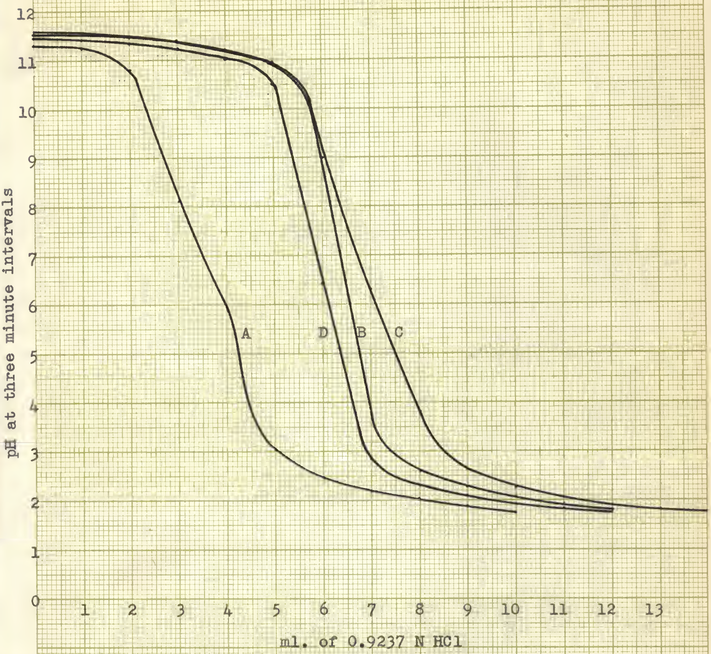
Legend:

A. Polymer of hexaallyl ethylenediammonium dibromide polymerized at 75°.

B. Polymer of hexaallyl ethylenediammonium dibromide polymerized at 70°.

C. Polymer of hexaallyl ethylenediammonium dibromide dried in the hydroxide form at 103° before titration.

GRAPH III.



Legend:

A. Polymer of triallyl butyl ammonium bromide.

B. Copolymer of diallyl piperidinium bromide and tetraallyl ammonium bromide.

C. Copolymer of diallyl morpholinium bromide and tetraallyl ammonium bromide.

D. Copolymer of triallyl butyl ammonium bromide and tetraallyl ammonium bromide.

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VI. DISCUSSION OF RESULTS

The procedure used for the preparation of the amines was found to give good yields. An average yield of 50% was obtained. The cost of production was reduced by letting the hydrogen bromide or hydrogen chloride eliminated in the reaction react with sodium bicarbonate instead of the more costly amines.

Acetophenone proved to be a good solvent for the preparation of the quaternary ammonium halides. Not only did the reaction proceed rapidly, but the solvent was easily extracted with ether. The hygroscopic nature of the quaternary ammonium halides is a disadvantage in large scale purification and storage.

The decomposition of the resins in the hydroxide form on drying prevents them from being distributed in that form. It would be necessary to convert them before use or to keep them wet after conversion. This disadvantage is found also in anion exchange resins now on the market.

The polymer of tetraallyl ammonium bromide has a relatively high capacity. The capacity calculated as grains of calcium carbonate per cubic foot is 21,000. This is the method of expressing the capacity in the water-softening field. This resin is stable in hot water, acids, and alkalies. The stability of the resin to these hot solutions would certainly be an advantage in operations carried out above room temperatures. The capacities of the other resins are decreased due to their swelling. If enough cross-linking could be introduced to prevent swelling of the resins their capacity per milliliter would be greatly increased.

From the experimental results obtained the different groups seem to have little effect on the capacity. The results are comparatively the same with the exception of triallyl butyl ammonium bromide. The low value of this resin is due to the large amount of swelling.

The results obtained in this study are of interest from two points of view. First, the polymerization of quaternary ammonium halides adds a new reaction to organic chemistry. Secondly, the resins produced surpass many of the present anion exchangers in capacity and compare favorably with the rest.

VII. SUMMARY

Twelve new unsaturated quaternary ammonium halides have been prepared and characterized. One additional compound of this type which was previously reported in disagreement with the present findings has been prepared and characterized.

As intermediates for the preparation of these quaternary compounds, seven new unsaturated tertiary amines have been prepared by the reaction of the appropriate secondary amines and alkyl halides in the presence of an aqueous solution of sodium bicarbonate. All these new amines have been characterized and their physical constants determined. Two other unsaturated tertiary amines which have been previously reported in literature without physical constants have been prepared and their physical constants determined.

The unsaturated quaternary ammonium halides have been polymerized by means of tertiary-butyl hydroperoxide to thermosetting polymers. It has been shown that all of the water insoluble polymers and copolymers will undergo ion exchange reactions as predicted.

The results obtained in this study have opened a new source for anion exchange resins.

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BIOGRAPHICAL ITEMS

Robert L. Bunch was born in Lincoln County, Kentucky on October 17, 1919. He pursued his undergraduate studies at Hanover College and was awarded the degree of Bachelor of Arts in June, 1943.

He entered the United States Air Corps in January, 1943 and after 42 months of active service was released to inactive duty in August, 1946.

At that time he undertook graduate studies in chemistry at the University of Illinois and was awarded the degree of Master of Arts in October, 1947.

In September, 1947 he entered the graduate school of the University of Florida and has been in attendance since that date.

Mr. Bunch is a member of Phi Delta Theta, Delta Epsilon, and the American Chemical Society.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date Sept. 3, 1949

T. M. Simpson
Dean

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D. B. Butler
Chairman

Paul Tarrant

W. R. Carroll

F. H. Heath.

L. R. Phillips